

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B32B 27/34, 27/08, C08L 77/00		A1	(11) International Publication Number: WO 98/29250
			(43) International Publication Date: 9 July 1998 (09.07.98)
(21) International Application Number: PCT/JP97/04787 (22) International Filing Date: 24 December 1997 (24.12.97)			(81) Designated States: BR, CN, JP, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(30) Priority Data: 8/357877 27 December 1996 (27.12.96) JP			Published <i>With international search report.</i>
(71) Applicant (<i>for all designated States except US</i>): KUREHA KAGAKU KOGYO K.K. [JP/JP]; 9-11, Nihonbashi Horidome-cho 1-chome, Chuo-ku, Tokyo 103 (JP).			
(72) Inventors; and (75) Inventors/Applicants (<i>for US only</i>): UEHARA, Tsutomu [JP/JP]; 3186-26, Shimoinayoshi, Chiyoda-machi, Niigaki-gun, Ibaraki 315 (JP). ISHII, Hitoshi [JP/JP]; 18-2, Kamitamari, Tamari-mura, Niigaki-gun, Ibaraki 311-34 (JP). TSUKAMOTO, Hajime [JP/JP]; 774, Kamitamari, Tamari-mura, Niigaki-gun, Ibaraki 311-34 (JP).			
(74) Agent: NISHIKAWA, Shigeaki; Visual City 401, 43-8, Higashi-Nippori 3-chome, Arakawa-ku, Tokyo 116 (JP).			

(54) Title: PACKAGING FILM OR SHEET

(57) Abstract

The invention provides a single-layer or multi-layer packaging film or sheet having at least one layer formed of a polyamide resin composition, wherein the layer formed of the polyamide resin composition is a layer (A) formed of a polyamide resin composition comprising a copolymer nylon (c) composed of an aliphatic nylon (co)polymer component (1) and an aromatic nylon (co)polymer component (2) in a proportion of at least 5 wt. %.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

DESCRIPTION

PACKAGING FILM OR SHEET

5 FIELD OF THE INVENTION

The present invention relates to a single-layer or multi-layer packaging film or sheet having a layer of a polyamide resin composition, and more particularly to packaging films or sheets which are well balanced among properties such as formability, heat shrinkability, gas barrier properties, softness and suitability for automatic packaging machines equipped with a sealing mechanism such as a high-frequency sealer.

The packaging films or sheets according to the present invention are particularly suitable for use as casing films, pillow packaging films or sheets and deep-draw packaging films or sheets for filling and packaging fluid or semifluid foods such as sausage and solid foods such as processed meat and ham.

20

BACKGROUND OF THE INVENTION

In recent years, remarkable technical innovation has been made in the field of food packaging, and packaging materials most suitable for packaging, preservation, shipment and the like of various foods have been always demanded. The development of an automatic packaging system has been advanced with a view toward

increasing production and reducing cost, and so the packaging materials are required to have excellent suitability for automatic packaging machines.

Single-layer or multi-layer films or sheets formed
5 of various kinds of synthetic resins are generally used
in the fields of casing films, pillow packaging films or
sheets and deep-draw packaging films or sheets for
filling and packaging fluid or semifluid foods, for
example, processed livestock products such as sausage,
10 processed marine products such as fish meat sausage, and
processed farm products and cooked products such as
devil's-tongue jelly and sweet rice jelly, and solid
products such as processed meat products and ham. For
example, films formed of a resin composition composed of
15 nylon and a polyolefin resin, or multi-layer laminated
films composed of a nylon layer and a polyolefin resin
layer are often used in the field of the casing films.

Of these films, a multi-layer laminated film composed of a nylon layer and a polyethylene layer (hereinafter referred to as "Ny/PE film") has good heat sealing property and gas barrier properties and is hence widely used. However, this Ny/PE film has involved a problem that it is lacking in softness. In addition, to the Ny/PE film, may be applied fin sealing (sealing surfaces being both the polyethylene layer) in which the polyethylene layer is used as sealing layers, but can not be applied the so-called overlap sealing (the sealing

surfaces being the nylon layer and polyethylene layer).

Therefore, the Ny/PE film can not be applied to any automatic filling and packaging machine equipped with an envelope-seam type sealing mechanism.

5 Several proposals have been made for polyamide resin compositions satisfying various properties as a casing film by a single layer. For example, in Japanese Patent Application Laid-Open No. 122732/1992, has been proposed a casing film formed from a mixture of nylon 6, 10 and an aromatic copolyamide (hereinafter referred to as "nylon 6I/6T") composed of a polycondensate of hexamethylenediamine with terephthalic acid and isophthalic acid. However, this casing film has involved difficulty in stably conducting blow stretching when this 15 casing film is produced by blown-film extrusion, because the internal stress of a tubular parison upon the blow stretching is high, so that the air pressure within a blown bubble becomes high, and bubble break often occurs. In addition, this casing film has also involved a problem 20 that when the casing film is filled with sausage in accordance with a method known *per se* in the art, boiled and then cooled, the wrinkles occur on the surface of the product, and the dimensions of the product become unstable. Further, the casing film has high stiffness, 25 so that working properties such as shirring and ease of filling are deteriorated.

When an aromatic nylon (hereinafter referred to as

"nylon MXD6") composed of adipic acid and m-xylylene-diamine is used in place of the nylon 6I/6T in the polyamide resin compositions, the above-described tendency becomes more pronounced. A film or sheet 5 obtained by blown-film extrusion using the nylon MXD6 involves difficulty in deep drawing it because when it is deep drawn, elongation of the film or sheet becomes uneven at portions corresponding to parts of from corners of the bottom to side walls of a deep-draw mold.

10

OBJECTS AND SUMMARY OF THE INVENTION

It is an object of the present invention to provide a single-layer or multi-layer packaging film or sheet having excellent formability, heat shrinkability, gas 15 barrier properties and softness.

Another object of the present invention is to provide a single-layer or multi-layer packaging film or sheet which has excellent ease of filling, causes no wrinkle and has excellent dimensional stability when it 20 is used as a casing film.

A further object of the present invention is to provide a single-layer or multi-layer packaging film or sheet which has such excellent properties as described above and is suitable for use as a casing film, a pillow 25 packaging film or sheet, or a deep-draw packaging film or sheet for packaging fluid or semifluid food, or solid food.

The present inventors have carried out an extensive investigation with a view toward overcoming the above-described problems involved in the prior art. As a result, it has been found that when a polyamide resin composition comprising a specific copolymer nylon is used for a single-layer or multi-layer packaging film or sheet having a layer formed of a polyamide resin composition, the above objects can be achieved.

The packaging films or sheets according to the present invention may be used in the form of a single-layer film or sheet, but may be used in the form of a multi-layer film or sheet by laminating it on other layers such as a polyolefin resin layer, as desired. The single-layer films composed of a layer of the polyamide resin composition according to the present invention or the multi-layer films having the layer of the polyamide resin composition as a surface layer have excellent suitability for automatic packaging machines equipped with a high-frequency sealing mechanism and may also be ultrasonically sealed.

The packaging films or sheets according to the present invention can be suitably used as heat shrinkable films, in particular, casing films when they are formed into oriented films. A multi-layer film or sheet obtained by laminating a polyolefin resin layer on the layer of the polyamide resin composition can be heat sealed by using the polyolefin resin layer as a sealing

surface. A single-layer or multi-layer tubular film or sheet obtained by blown-film extrusion can be used as a casing film as it is. Non-oriented packaging films or sheets according to the present invention have excellent 5 suitability for automatic packaging machines and deep drawing property and are suitable for use as films or sheets for pillow packaging (i.e., flow-pack) and deep-draw packaging (i.e., thermo-forming).

The present invention has been led to completion on 10 the basis of these findings.

According to the present invention, there is thus provided a single-layer or multi-layer packaging film or sheet having at least one layer formed of a polyamide resin composition, wherein the layer formed of the 15 polyamide resin composition is a layer (A) formed of a polyamide resin composition comprising a copolymer nylon (c) composed of an aliphatic nylon (co)polymer component (1) and an aromatic nylon (co)polymer component (2) in a proportion of at least 5 wt.%.

20

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Copolymer nylon (c):

In the present invention, as a polyamide resin composition for forming the polyamide resin composition 25 layer (A), is used a polyamide resin composition comprising a copolymer nylon (c) composed of an aliphatic nylon (co)polymer component (1) and an aromatic nylon

(co)polymer component (2) in a proportion of at least 5 wt.%.

Examples of the aliphatic nylon (co)polymer component (1) include nylon 6, nylon 11, nylon 12, nylon 5 66, nylon 69, nylon 610, nylon 6/66 and nylon 6/12. Of these, at least one aliphatic nylon (co)polymer component selected from the group consisting of the components of nylon 6, nylon 66 and nylon 610 is preferred. Particularly, nylon 6/12, nylon 66/69, nylon 66/610 and 10 nylon 610 are more preferred.

As the aromatic nylon (co)polymer component (2), is preferably used that having an aromatic diamine unit or that having an aromatic dicarboxylic acid unit. Specific examples thereof include xylylene type polyamides. The 15 xylylene type polyamides are polyamide resins synthesized by a polycondensation reaction of m-xylylenediamine alone or a diamine mixture of m-xylylenediamine in an amount of at least 60 wt.%, preferably at least 70 wt.% and p-xylylenediamine in an amount of at most 40 wt.%, 20 preferably at most 30 wt.% with an aliphatic dibasic acid having 6-12 of carbon atoms, for example, adipic acid, sebacic acid, suberic acid, undecanedioic acid or dodecanedioic acid. More specific examples thereof include homopolymers such as poly(m-xylylene adipamide), 25 poly(m-xylylene sebacamide) and poly(m-xylylene suberamide), m-xylylene/p-xylylene adipamide copolymers, m-xylylene/p-xylylene pimelamide copolymers, m-

xylylene/p-xylylene azelamide copolymers, and m-xylylene/p-xylylene adipamide/sebacamide copolymers. Of these, poly(m-xylylene adipamide) (MXD6) is preferred.

Other examples of the aromatic nylon (co)polymer component (2) include polycondensates of hexamethylene-diamine with at least one aromatic dicarboxylic acid selected from the group consisting of terephthalic acid and isophthalic acid.

A proportion of the aromatic nylon (co)polymer component (2) to be copolymerized in the copolymer nylon (c) is preferably at most 40 wt.% from the viewpoints of formability, heat shrinkability, gas barrier properties and softness.

Preferable examples of the copolymer nylon (c) include copolymer nylons comprising ① 45-92 wt.% of a nylon 6 component and ② 4-25 wt.% of another aliphatic nylon component than the nylon 6 component as the aliphatic nylon (co)polymer component, and ③ 4-40 wt.% of an aromatic nylon component containing a xylylenediamine unit as the aromatic nylon (co)polymer component. A specific example thereof includes nylon 6/12/MXD6.

Other preferable examples of the copolymer nylon (c) include copolymer nylons comprising ① 60-96 wt.% of a nylon 610 component or a nylon 66/610 component as the aliphatic nylon (co)polymer component and ② 4-40 wt.% of an aromatic nylon component containing a xylylenediamine

unit as the aromatic nylon (co)polymer component.

Specific examples thereof include nylon 610/MXD6 and nylon 66/610/MXD6.

Further examples of the copolymer nylon (c) include
5 copolymer nylons comprising ① 60-96 wt.% of a nylon 6 component or a nylon 66/69 component as the aliphatic nylon (co)polymer component and ② 4-40 wt.% of a polycondensate component of hexamethylenediamine with at least one aromatic dicarboxylic acid selected from the
10 group consisting of isophthalic acid and terephthalic acid as the aromatic nylon (co)polymer component.

Specific examples thereof include nylon 6/6I and nylon 66/69/6I.

The copolymer nylon (c) used in the present
15 invention is a crystalline polyamide and generally has a crystallization velocity, $\tau_{1/2}$, of 20 seconds or longer. When the so-called hot stretching, in which a polyamide resin composition is heated to 70-95°C to stretch it, is conducted, the incorporation of the copolymer nylon (c)
20 into the polyamide resin composition permits slowing the crystallization velocity of the polyamide resin composition to facilitate the operation of the hot stretching. Namely, the copolymer nylon (c) contributes to the improvement of stretchability, film-forming
25 property and high-frequency sealing property. This copolymer nylon also permits improvement in the softness of a film or sheet formed, thereby improving its ease of

filling with sausage or the like and further its secondary processing characteristics or properties such as suitability for stirring, ring-forming property, ease of film cutting, suitability for pillow packaging
5 machines and deep-drawing property. The copolymer nylon improves the gas barrier properties of the film or sheet to some extent. Any blend of an aliphatic nylon such as nylon 6 and an aromatic nylon, not the copolymer nylon, cannot well balance these features with one another.

10 A proportion of the aromatic nylon (co)polymer component (2) such as nylon MXD6 to be copolymerized in the copolymer nylon (c) is at most 40 wt.%, preferably 4-40 wt.%. If the proportion is too low, the oxygen gas barrier property of the resulting film or sheet is lowered. If the proportion is too high on the other hand, the stiffness of the film or sheet becomes too high, and so its softness is impaired. If a proportion of the aliphatic nylon (co)polymer component (1) to be copolymerized in the copolymer nylon (c) is too low, the 15 softness of the resulting film or sheet is impaired. If the proportion is too high on the other hand, the effects of improving the oxygen transmission rate and water vapor transmission rate of the film or sheet are lessened.
20

In the copolymer nylon (c) having a copolymerization composition of aliphatic nylon/another aliphatic nylon/ aromatic nylon copolymer such as the 25 nylon 6/12/MXD6 and the nylon 66/610/MXD6, the presence

of another aliphatic nylon component permits improvement in the softness of the resulting film or sheet. When the ordinary nylon MXD6 is used in place of the specific copolymer nylon, the resulting film becomes poor in 5 softness and stretchability, is too hard to achieve good suitability for stirring as a casing film for packaging a pasty substance such as sausage, and is also not very improved in dimensional stability.

A proportion of the copolymer nylon (c) to be 10 incorporated into the polyamide resin composition is at least 5 wt.%, preferably 5-40 wt.%, more preferably 5-30 wt.%. If the proportion is too low, the effect of slowing the crystallization velocity of the polyamide resin composition is lessened. If the proportion is too 15 high on the other hand, the resulting film becomes too soft, so that when a casing film composed of such a film is filled with sausage or the like, the film is elongated by the filling pressure, and so the dimensions and form of the resulting product vary, and the dimensional 20 stability and form stability of the product are impaired. Even if the proportion of the copolymer nylon (c) exceeds 40 wt.%, such various properties are easy to be well balanced when a layer of such a composition is laminated on a layer of another polyamide resin than this, for 25 example, an aliphatic (co)polymer nylon or nylon MXD6.

Polyamide resin composition:

According to the present invention, in a single-

layer or multi-layer packaging film or sheet having at least one layer formed of a polyamide resin composition, a polyamide resin composition comprising the copolymer nylon (c) in a proportion of at least 5 wt.% is used as 5 the polyamide resin composition for forming the layer of the polyamide resin composition. The polyamide resin composition comprises at least 5 wt.% of the copolymer nylon (c) and at most 95 wt.% of another nylon (co)polymer than the copolymer nylon (c), and as needed, 10 any other resin component such as an amorphous nylon (b) and/or a polyolefin resin may be blended therewith within the limits of a minor amount.

As the polyamide resin composition, is preferred a polyamide resin composition comprising 40-70 wt.% of 15 nylon 6 (a), 5-20 wt.% of an amorphous nylon (b), 5-30 wt.% of the copolymer nylon (c) and 10-30 wt.% of a polyolefin resin (d).

Besides, a polyamide resin composition comprising 20 50-95 wt.% of nylon 6 (a) and 5-50 wt.% of the copolymer nylon (c) may be used as the polyamide resin composition. Further, a polyamide resin composition comprising 50-95 wt.% of nylon MXD6 (e) and 5-50 wt.% of the copolymer nylon (c) may preferably be used as the polyamide resin composition.

25 Nylon 6:

Nylon 6 (Ny 6) in the polyamide resin composition is concerned in the balance between film-forming property

and oxygen gas barrier property. A proportion of nylon 6 to be incorporated may be suitably determined according to other blending components. In a polyamide resin composition comprising nylon 6 (a), an amorphous nylon 5 (b), the copolymer nylon (c) and a polyolefin resin (d), however, the proportion of the nylon 6 is generally 40-70 wt.%, preferably 50-70 wt.%.

In a polyamide resin composition comprising nylon 6 (a) and the copolymer nylon (c), the proportion of the 10 nylon 6 is generally 50-95 wt.%, preferably 40-95 wt.%. Accordingly, the proportion of the copolymer nylon (c) is generally 5-50 wt.%, preferably 5-40 wt.%.

If the proportion of nylon 6 is too high, the oxygen transmission rate and water vapor transmission 15 rate of the resulting oriented film are lowered. If the proportion is too low on the other hand, the stretchability upon the formation of a blown film is lowered.

Amorphous nylon:

20 The amorphous nylon in the polyamide resin composition is a polyamide having an aromatic ring in its main chain and/or side chain and having no crystallinity or very low crystallinity. Specific examples thereof include polycondensates of a dicarboxylic acid such as 25 terephthalic acid or isophthalic acid with a diamine such as hexamethylenediamine or copolymers thereof. For example, polyamides (nylon 6I/6T) obtained by

polycondensing a dicarboxylic acid component composed of 10-50 wt.% of terephthalic acid and 90-50 wt.% of isophthalic acid with hexamethylenediamine may be mentioned.

5 The stretchability and oxygen gas barrier property of the polyamide resin composition is affected by the range of the amorphous nylon in the polyamide resin composition. A proportion of the amorphous nylon to be incorporated in the polyamide resin composition is
10 generally 5-20 wt.%, preferably 5-15 wt.%. If the proportion of the amorphous nylon is too high, the stiffness of the resulting film becomes high, and so its softness is lowered. If a film does not have sufficient softness, difficulty is encountered on handling when the
15 film is put to practical use as a casing film to fill it with sausage or the like, and since suitability for shirring and ring-forming property are deteriorated, or the life of a cutter for cutting the film is shortened, problems arise on secondary processing properties of the
20 film. When it is combined with a specific copolymer composition, these properties are easy to be well balanced. If the proportion of the amorphous nylon is too low, it is difficult to satisfactorily retain the form of the resulting film.

25 Polyolefin resin:

Examples of the polyolefin resin used in the present invention include homopolymers of ethylene and

α -olefins, such as high density polyethylene, medium density polyethylene, low density polyethylene and polypropylene; ethylene- α -olefin copolymers (for example, copolymers obtained by using a metallocene catalyst, such as AFFINITY™) such as linear low density polyethylene (LLDPE) and very low density polyethylene (VLDPE); and besides ionomer resins, polyamide-modified ionomer resins, ethylene-vinyl acetate copolymers, ethylene-ethyl acrylate copolymers, ethylene-acrylic acid copolymers, 10 ethylene-methyl acrylate copolymers, ethylene-methyl methacrylate copolymers and ethylene-methacrylic acid copolymers. These polyolefin resins may be used either singly or in any combination thereof.

As the polyolefin resin mixed with the polyamide resin composition, ethylene copolymers such as ethylene-acrylic acid copolymers and ethylene-methacrylic acid copolymers, and polyamide-modified ionomer resins are preferred from the viewpoint of compatibility with the individual polyamide components.

20 The polyamide-modified ionomer resins are resins obtained by ionizing a copolymer of ethylene and an α,β -unsaturated carboxylic acid with a metal ion such as zinc, lithium, potassium, magnesium, calcium or sodium ion to prepare an ionomer, adding a polyamide to the ionomer and 25 melting and kneading the resultant mixture at a high temperature of 200-350°C to modify the ionomer. Examples of the polyamide used herein include nylon 6, nylon 66,

nylon 6/66, nylon 6/10, nylon 6/12, nylon 11, nylon 12 and mixture of two or more of these polyamides. Of these, nylon 6 and copolymers thereof are preferred.

A proportion of the polyolefin resin to be
5 incorporated in the polyamide resin composition is generally 10-30 wt.%. If the proportion of the polyolefin resin is too low, the water vapor transmission rate of the resulting film becomes too high, so that loss in weight of the contents in a packaged product becomes
10 great when sausage or the like is packaged with the film to store it. If the proportion is too high, the stretchability of the resulting film is deteriorated, and moreover its oxygen transmission rate is increased, so that the contents in a product packaged with the film
15 tend to undergo putrefaction due to oxidative deterioration.

Film or sheet:

The polyamide resin composition useful in the practice of the present invention can be prepared by
20 mixing the individual components by a method known *per se* in the art. For example, raw materials such as pellets, granules, powders or the like of the individual polymers are mixed upon the formation of a film or sheet, whereby a uniform composition can be prepared. To the polyamide resin composition, may be added various additives such as a plasticizer, a stabilizer, a lubricant, an antioxidant, a pigment and a dye, as needed, within limits not

impairing the properties of the resulting film.

No particular limitation is imposed on the film-forming process. For example, T-die extrusion or blown-film extrusion may be used. The blown-film extrusion is generally used. The melting temperature of each resin is generally 300°C or lower, preferably 240-280°C, more preferably 240-260°C. A non-oriented film obtained by the T-die extrusion is biaxially oriented simultaneously or successively at an orientation temperature of 120°C or lower by a tenter process. A tubular parison obtained by the blown-film extrusion is biaxially oriented by blowing air into the parison at an orientation temperature of 120°C or lower to inflate it. The draw ratio is generally 2.0-10.0 times, preferably 2.2-8.0 times, more preferably 2.2-5.0 times in each of machine and transversal directions. Moderate heat shrinkability and dimensional stability such as creep characteristics are achieved by the orientation.

The thickness of the film according to the present invention is generally 10-100 µm, preferably 10-50 µm, more preferably 20-40 µm in the case of a singly-layer film. A thickness too small is not preferable because the oxygen gas barrier property and water vapor barrier property of the film are lowered. A thickness too great is also not preferable because the stiffness of the film becomes too high, and so its softness is deteriorated. In the case of a multi-layer film, the film is used in a

thickness ranging from 10 to 250 μm .

In the packaging of processed meat products, packaged products such as sausage dislike wrinkling from the viewpoint of the aesthetic appearance of the products.

- 5 In order to prevent the products from wrinkling, it is necessary for the film to shrink under heat upon boiling or sterilization treatment so as to keep it tense. The oriented films according to the present invention have a shrink (hot-water shrink) of generally at least 5%,
- 10 preferably at least 8%, more preferably at least 10% in each of longitudinal and transversal directions when immersed in hot water of 80°C.

The films according to the present invention preferably have a haze of at most 20%. Since the haze of 15 the films is low, the contents such as sausage can be visually seen from the outside of the packaging film.

- 20 The films or sheets according to the present invention have an oxygen transmission rate (in terms of the thickness of 35 μm) of $300 \text{ cm}^3/\text{m}^2 \cdot \text{day} \cdot \text{atm}$ or smaller, preferably $200 \text{ cm}^3/\text{m}^2 \cdot \text{day} \cdot \text{atm}$ or smaller as measured at a temperature of 30°C and 100% RH (relative humidity) and a water vapor transmission rate of preferably $70 \text{ g/m}^2 \cdot \text{day}$ or smaller as measured at a temperature of 40°C and 90% RH, so that when a food product packaged with the film is 25 stored for a long period of time, putrefaction of the contents by oxygen and loss in weight of water can be prevented, and the flavor and taste of the contents can

be retained.

If the hot-water shrink of the casing film according to the present invention is lower than 5% at 80°C, a product obtained by filling the casing film with, for example, fluid or semifluid sausage wrinkles in its surface after boiling it. Therefore, such a low hot-water shrink is not preferable.

Hot-water creep at 80°C for 10 seconds may be used as an evaluation standard for the dimensional stability of the films. The oriented films according to the present invention preferably have a hot-water creep of at most 20%, more preferably at most 18%. If the hot-water creep of the film is too high, a dimensional scatter of a packaged product obtained by filling with, for example, sausage becomes too wide after boiling the package. Therefore, such a too high hot-water creep is not preferable.

The films or sheets according to the present invention have excellent high-frequency sealing property. A number of films formed of a resin composition composed of a polyamide and a polyolefin resin and/or the like have heretofore been proposed and used. However, none of them are not particularly referred to the high-frequency sealing property. The present inventors have carried out an extensive investigation as to this sealing property. As a result, it has been found that when a film formed of a polyamide alone, for example, a film of nylon 6, is

subjected to high-frequency sealing by an automatic filling and packaging machine (Automatic Filling and Packaging Machine KAP manufactured by Kureha Chemical Industry Co., Ltd.), discharge occurs at the sealed portion, and so good sealing property cannot be achieved.

On the other hand, even when a film or sheet formed of the polyamide resin composition according to the present invention is subjected to high-frequency sealing by means of an automatic filling and packaging machine equipped with a high-frequency sealing mechanism, stable sealing can be continuously conducted without discharge. The films or sheets according to the present invention have not only excellent high-frequency sealing property but also good heat sealing property and ultrasonic sealing property.

The films or sheets according to the present invention may be used in the form of a single-layer film or sheet, but may be used in the form of a multi-layer film or sheet by laminating it on, for example, at least one polyolefin resin layer (may be combined with an adhesive resin layer) by co-extrusion or lamination in order to impart or improve heat sealing property.

More specifically, examples of the multi-layer film or sheet include multi-layer films or sheets having a laminated structure of at least 3 layers with an adhesive resin layer (B) and a polyolefin resin layer (C) laminated on a layer (A) of the polyamide resin

composition in suitable combinations, for example, A/B/C, A/C/A, A/B/A, C/A/C, A/B/C/B/A and C/B/A/B/C. Additional resin layers may be provided as desired. Of these, the multi-layer film or sheet having a layer (A) of the 5 polyamide rein compositon as a surface layer can be applied to high-frequency sealing.

Examples of the polyolefin resin include homopolymers such as low density polyethylene (LDPE), medium density polyethylene (MDPE), high density 10 polyethylene (HDPE) and polypropylene; ethylene- α -olefin copolymers (for example, copolymers obtained by using a metallocene catalyst, such as AFFINITYTM; particularly, those having a density of 0.900 g/cm³ or higher) such as linear low density polyethylene (LLDPE) and very low 15 density polyethylene (VLDPE); ethylene copolymers such as ethylene-vinyl acetate copolymers (EVA), ethylene-ethyl acrylate copolymers (EEA), ethylene-methacrylic acid copolymers (EMA), ethylene-acrylic acid copolymers (EAA) and ionomer resins; and mixtures composed of two or more 20 of these polymers.

Examples of the adhesive resin include modified polymers obtained by graft-copolymerizing an unsaturated carboxylic acid such as maleic acid, fumaric acid or acrylic acid, or an anhydride or ester thereof with 25 homopolymers or copolymers of olefins, such as polyethylene resins (including α -olefin resins such as LLDPE and VLDPE), polypropylene, polybutene, copolymers

of these comonomers with each other, ionomer resins, ethylene-acrylic acid copolymers and ethylene-vinyl acetate copolymers; and mixtures of two or more of these graft copolymers.

5 Examples of other resin layers and additional resin layers include a layer formed of a saponified product (EVOH) of an ethylene-vinyl acetate copolymer, and layers formed of gas barrier resins such as nylon MXD6. These gas barrier resin layers are generally provided as an
10 intermediate layer in the multi-layer films or sheets. In this case, in order to enhance the film-forming property and stretchability of the gas barrier resin, it is preferable that ① the gas barrier resin layer be provided in adjacency with the polyamide resin
15 composition layer (A), ② the gas barrier resin layer be provided between two layers (A) of the polyamide resin composition, or ③ in the case of nylon MXD6, it be blended with the copolymer nylon (c) to use the blend to form a polyamide resin composition layer (A).

20 As other resin layers and additional resin layers, may also be mentioned layers of other polyamide resins and layers of polyethylene terephthalate resins.

As the multi-layer packaging films or sheets according to the present invention, may be mentioned
25 multi-layer oriented films or sheets comprising at least one polyamide resin composition layer (A), and multi-layer non-oriented films or sheets comprising at least

one polyamide resin composition layer (A).

Specifically, multi-layer packaging films or sheets comprising at least one polyamide resin composition layer (A) as an intermediate layer may be mentioned. More

5 specifically, multi-layer packaging films or sheets comprising at least one polyamide resin composition layer (A) as an intermediate layer and polyolefin resin layers as the outermost layer and the innermost layer through adhesive layers may be mentioned.

10 Besides, multi-layer packaging films or sheets comprising at least one polyamide resin composition layer (A) as an intermediate layer, a polyethylene terephthalate resin layer as one surface layer through an adhesive layer, and a polyolefin resin layer as the other

15 surface layer through an adhesive layer may be mentioned.

In order to control the slip property of the resulting multi-layer film or sheet, silica particles may be added to the polyethylene terephthalate resin of the surface layer. As a method for adding the silica particles,

20 there is a method in which 2.5 wt.% of silica particles are blended with 97.5 wt.% of a polyethylene terephthalate resin to prepare a lubricant, and the lubricant is added to a polyethylene terephthalate resin.

If the concentration of the silica particles in the resin 25 is 1,000 ppm or higher, the suitability of the resulting film or sheet for pillow packaging becomes poor.

Therefore, it is preferable to control the concentration

to generally about 200-800 ppm, more preferably about 500 ppm. A multi-layer film or sheet comprising, as a surface layer, the polyethylene terephthalate resin layer the slide property of which has been controlled as 5 described above has far excellent suitability for pillow packaging.

Examples of the intermediate layer include ① a layer having a layer structure composed of at least one polyamide resin composition layer (A) and at least one 10 polyamide layer laminated in adjacency with each other, and ② a layer having a layer structure composed of at least one polyamide resin composition layer (A) and at least one gas barrier resin layer laminated in adjacency with each other.

15 Multi-layer packaging films or sheets comprising at least one polyamide resin composition layer (A) as at least one surface layer may be mentioned. In this case, a polyolefin resin layer may be provided as an intermediate layer, or a layer of another polyamide resin 20 (including another polyamide resin composition) may be provided as the other surface layer. More specifically, multi-layer packaging films or sheet comprising a polyamide resin composition layer (A) as one surface layer, and a polyamide resin layer as the other surface 25 layer may be mentioned.

Multi-layer packaging films or sheets having a layer structure composed of at least two layers of a

layer formed of the copolymer nylon (c) composed of the aliphatic nylon (co)polymer component (1) and the aromatic nylon (co)polymer component (2), and a layer formed of another polyamide than the copolymer nylon (c)

5 in adjacency with each other may also exhibit good various properties. Examples of thereof include aliphatic nylon (co)polymer layer/adhesive resin layer/copolymer nylon (c) layer/adhesive resin layer/polyethylene layer, mixed layer of aliphatic nylon

10 (co)polymer and amorphous nylon (b)/adhesive layer/copolymer nylon (c) layer/adhesive resin layer/mixed layer of polyethylene and anti-clouding agent.

Multi-layer packaging films or sheets having a layer structure composed of at least two layers of a

15 layer formed of the polyamide resin composition comprising the copolymer nylon (c) composed of the aliphatic nylon (co)polymer component (1) and the aromatic nylon (co)polymer component (2) having an aromatic diamine unit, and at least one layer of a layer

20 formed of another polyamide resin composition than the above composition and a gas barrier resin layer may also exhibit good various properties.

The single-layer or multi-layer oriented films or sheets according to the present invention can be suitably

25 used as casing films. Since the films or sheets comprising the polyamide resin composition according to the present invention are good in film-forming property

and stretchability upon the formation of the films or sheets and have moderately balanced properties among softness, hot-water shrink, creep property, toughness, gas barrier properties, dimensional stability,

- 5 suitability for automatic packaging machines and the like, they are suitable for casing films for filling and packaging fluid or semifluid foods, for example, processed livestock products such as ham and sausage, processed marine products such as fish meat sausage, and
10 processed farm products and cooked products such as devil's-tongue jelly and sweet rice jelly.

The single-layer or multi-layer non-oriented films or sheet according to the present invention are suitably used as films or sheets for deep-draw packaging and
15 pillow packaging.

Blow molded container:

The polyamide resin composition comprising a copolymer nylon (c) composed of an aliphatic nylon (co)polymer component (1) and an aromatic nylon
20 (co)polymer component (2) in a proportion of at least 5 wt.%, and the copolymer nylon (c) itself have excellent moldability, are easy to form a uniform section, and can be suitably used in stretch blow molding in particular.

- Therefore, according to the present invention,
25 there are provided single-layer or multi-layer blow molded containers having at least one layer formed of a polyamide resin composition, wherein the layer formed of

the polyamide resin composition is a layer (A) formed of a polyamide resin composition comprising a copolymer nylon (c) composed of an aliphatic nylon (co)polymer component (1) and an aromatic nylon (co)polymer component 5 (2) in a proportion of at least 5 wt.%, or of the copolymer nylon (c) alone.

ADVANTAGES OF THE INVENTION

According to the present invention, there are 10 provided single-layer or multi-layer packaging films or sheets having excellent formability, heat shrinkability, gas barrier properties, softness and suitability for automatic packaging machines equipped with a sealing mechanism such as a high-frequency sealer, heat sealer or 15 ultrasonic sealer. The packaging films or sheets according to the present invention are suitable for use as casing films, pillow packaging films or sheets and deep-draw packaging films or sheets for filling and packaging fluid or semifluid foods such as sausage and 20 solid foods such as processed meat and ham.

EMBODIMENTS OF THE INVENTION

The present invention will hereinafter be described more specifically by the following Examples and Comparative Examples. Incidentally, various physical 25 properties in the examples were measured in accordance with the following respective methods.

(1) Crystalline melting point (T_m):

The crystalline melting point of each sample was measured by means of a DSC7 (trade name) manufactured by Perkin Elmer Company. The measurement was conducted in the following manner. Namely, 5-10 mg of a sample resin 5 were weighed out, and the resin was melted once and held for 2 minutes at a temperature higher than the melting point at this time by 40°C. Thereafter, the resin was quenched to 0°C at a rate of 200°C/min and held for 2 minutes. The resin was then heated at a rate of 20°C/min, 10 and a melting peak temperature in this process was regarded as the crystalline melting point.

(2) Stretchability (formability upon the formation of an oriented film):

A tubular parison was produced with a resin 15 composition sample by blown-film extrusion, and air was blown into the parison to inflate and stretch it, thereby evaluating the sample as to stretchability in accordance with the following standard:

- : The parison was could be continuously stretched 20 with extremely little breaking of the bubble;
- △: Breaking of the bubble sometimes occurred (about once in 8 hours); and
- ×: Breaking of the bubble frequently occurred (at least two or three times in 8 hours).

25 (3) Shrinkage:

A sample film was immersed for 10 seconds in hot water of 80°C, and a shrinkage of the film in each of

longitudinal and transversal directions was then determined.

(4) Creep:

A sample film was immersed for 10 seconds in hot
5 water of 80°C, and a creep of the film was then determined.

(5) Oxygen transmission rate:

The oxygen transmission rate of a sample film was measured by means of MOCON OXTRAN-100 MODEL (trade name)
10 manufactured by MODERN CONTROL Co. under conditions of 30°C and 100% RH in accordance with ASTM D 3985-81.

(6) Water vapor transmission rate:

The water vapor transmission rate of a sample film was measured by means of VAPOR PERMEATION TESTER-400
15 (trade name) manufactured by LYSSY Co. under conditions of 40°C and 90% RH.

(7) Overfill rate (maximum fill rate):

A sample casing film was filled with sausage, thereby determining a maximum overfill rate at this time.

20 (8) Ease of filling:

Upon the determination of the overfill rate, the ease of filling of the sample casing film was evaluated in accordance with the following standard:

○: Sausage in the form of semifluid could be
25 smoothly filled into the casing film;

△: The casing film was hard, and its shirring and filling thereinto were hence difficult; and

× : The casing film was elongated, and the dimension in the diametric direction thereof was difficult to retain.

(9) Wrinkling tendency:

5 A sample tubular oriented film was filled with sausage, and the resultant product was boiled for 60 minutes in hot water of 80°C and immediately cooled in cold water of 5°C, thereby visually observing it and evaluating the film as to the wrinkling tendency in
10 accordance with the following standard:

○: No wrinkle occurred; and

×: Wrinkles occurred.

[Example 1]

Mixed with 56 wt.% of nylon 6 (AMILAN CM1021XF,
15 trade name, product of Toray Industries, Inc.) were 12 wt.% of amorphous nylon (GRIVORY G21, trade name, product of EMS Chemical AG.), 12 wt.% of nylon 6/12/MXD6 (molar ratio of the comonomers: 72/8/20; Tm: 168°C), 10 wt.% of polyethylene (SUMIKATHENE F114-1, trade name, product of
20 Sumitomo Chemical Co., Ltd.; Tm: 106°C) and 10 wt.% of an ethylene-acrylic acid copolymer (ESCOR TR5001, trade name, product of EXXON Chemical Co.; Tm: 102°C; acrylic acid content: 6%), and the resultant mixture was melted and extruded at 245°C by means of a twin-screw extruder (BT-
25 30, trade name, manufactured by Plastic Kogaku Kenkyusho K.K.). A molten resin extruded through a ring die was immediately quenched in water of 15°C to obtain a tubular

parison.

After this parison was heated in hot water of 90°C, air was immediately blown into the parison to inflate and stretch it at draw ratios of 3.1 times and 4.1 times in

- 5 longitudinal and transversal directions, respectively, by the air pressure, thereby obtaining a tubular oriented film having a thickness of 35 µm and a width of 70 mm. The formability (stretchability) upon the formation of this oriented film, and the shrink, creep, oxygen
10 transmission rate and water vapor transmission rate of the resultant film, as well as the maximum overfill rate and ease of filling upon filling with sausage and wrinkling tendency after boiling and cooling as properties in practical use were separately evaluated.
15 The results are shown in Table 1.

[Example 2]

An oriented film was produced and evaluated in the same manner as in Example 1 except that nylon 610/MXD6 (molar ratio of the comonomers: 80/20; Tm: 173°C) was

- 20 used as the copolymer nylon in place of nylon 6/12/MXD6. The results are shown in Table 1.

[Comparative Examples 1-3]

Oriented film were produced and evaluated in the same manner as in Example 1 except that their

- 25 corresponding resin compositions shown in Table 1 were separately used. The results are shown in Table 1.

Table 1

		Example		Comp. Ex.		
		1	2	1	2	3
Compo- sition (wt.%)	Nylon 6	56	56	56	-	56
	Amorphous nylon	12	12	24	24	12
	Nylon 6/12/MXD6	12	-	-	-	-
	Nylon 610/MXD6	-	12	-	-	-
	Nylon 6/66	-	-	-	56	-
	MXD6	-	-	-	-	12
	PE	10	10	10	10	10
	EAA	10	10	10	10	10
Film proper- ties	Stretchability	○	○	×	○	△
	Shrinkage (%)	L direction	14	13	10	11
		T direction	12	12	9	10
	Creep (%)	L direction	16	17	16	21
		T direction	10	10	3	8
	Oxygen transmission rate (cm ³ /m ² ·day·atm)	174	185	146	228	142
	water vapor transmission rate (g/m ² ·day)	43	45	39	54	36
	Overfill rate (%)	15	16	10	23	10
	Ease of filling	○	○	△	×	△
	Wrinkling tendency	○	○	×	○	×

It is understood from the results shown in Table 1
that the oriented films according to the present

invention have stable stretchability and various properties and further have excellent performance in practical use as casing films.

[Examples 3-5]

- 5 Oriented films were produced and evaluated in the same manner as in Example 1 except that the same resins as those used in Example 1 are used, but their corresponding resin compositions shown in Table 2 are separately used.

Table 2

		Example			
		3	4	5	
Compo- sition (wt.%)	Nylon 6	50	62	68	
	Amorphous nylon	10	10	8	
	Nylon 6/12/MXD6	20	8	8	
	PE	10	10	8	
	EAA	10	10	8	
Film proper- ties	Stretchability	○	○	○	
	Shrinkage (%)	L direction	14	14	13
		T direction	13	13	11
	Creep (%)	L direction	17	15	12
		T direction	8	8	7
	Oxygen transmission rate (cm ³ /m ² ·day·atm)	190	160	200	
	water vapor transmission rate (g/m ² ·day)	45	42	49	
	Overfill rate (%)	16	15	15	
	Ease of filling	○	○	○	
	Wrinkling tendency	○	○	○	

It is understood from the results shown in Table 2 that the oriented films according to the present invention are well balanced among properties such as stretchability, shrinkability and gas barrier properties and have excellent performance in practical use as casing.

films.

[Example 6]

The oriented film obtained in Example 2 was used as a casing film as it is, and filled with 300 g of pork sausage at a fill rate of 10%, thereby producing 100 filled products. These products were boiled for 60 minutes in hot water of 80°C, and then immediately cooled in cold water of 5°C. After the packages were kept for a day at 5°C in a refrigerator, their dimensions were measured. Dimensional scatters in length and perimeter are shown in Table 3. It is understood that the dimensional scatters of the packages according to the present invention are narrow.

[Comparative Example 4]

Pork sausage was filled in the same manner as in Example 6 except that the tubular oriented film obtained in Comparative Example 1 was used as the casing film, and the resultant packages were evaluated in the same manner. The results are shown in Table 3. However, when this casing film was used and filled with the sausage at a fill rate of 10%, any package could not be stably obtained.

[Comparative Example 5]

Pork sausage was filled in the same manner as in Example 6 except that the tubular oriented film obtained in Comparative Example 2 was used as the casing film, and the resultant packages were evaluated in the same manner.

The results are shown in Table 3. The dimensional scatters of the resultant packages were wide in both length and perimeter.

Table 3

	Dimensional scatter of packaged sausage (%)	
	Longitudinal direction	Transversal direction
Example 6	3.0	2.8
Comp. Ex. 4	-	-
Comp. Ex. 5	8.3	11.7

5

[Example 7]

A tubular oriented film having a width of 250 mm was produced in the same manner as in Example 2 and then slit into flat films having a width of 90 mm. The flat 10 film was used to conduct a bag-making experiment by means of an automatic filling and packaging machine (KAP500 Model, trade name, manufactured by Kureha Chemical Industry Co., Ltd.). Specifically, bag-making properties such as slip property at forming parts and high-frequency 15 sealability are evaluated under conditions of a width between folds of 38 mm and a bag-making speed of 15 m/min. As a result, it was found that the film has stable and good suitability for automatic packaging.

[Example 8]

20 VLDPE (EXCELLEN VL401, trade name, product of Sumitomo Chemical Co., Ltd.), an adhesive resin (SF730,

trade name, product of Mitsui petrochemical Industries, Ltd.), nylon 6/66 (AMILAN CM6241M, trade name, product of Toray Industries, Inc.) and nylon 6/6I (SNIAMID F36T, trade name, product of Caffaro Co., LTD., Tm: 220°C) were 5 co-extruded into a tube having the following layer structure by means of 4 extruders, thereby obtaining a cold parison (non-oriented multi-layer tube). The cold parison was then heated again and stretched each 2.5 times in machine and transversal directions by an 10 inflation method. The thus-obtained tubular film was cut in the take-up direction of the film, thereby obtaining a film having a width between folds of 450 mm. This film was seamed at its center by an overlap sealing to produce a casing film. Processed meat was then filled into the 15 casing film, and the package was heated at 90°C for 1 minutes to shrink the film. As a result, it was found that the film beautifully fits on the processed meat, and its edges are soft to the touch and do not damage fingertips.

20 The layer structure of the film was as follows:
outer layer (VLDPE; 10 µm)/adhesive layer (1 µm)/
intermediate layer (nylon 6/66; 12 µm)/intermediate layer
(nylon 6/6I; 6 µm)/adhesive layer (1 µm)/inner layer
(VLDPE; 18 µm).

25 This multi-layer film had good stretchability (rank: ○), an oxygen transmission rate of 250 cm³/m²·day·atm and hot-water shrinks of 27% and 26% in

longitudinal and transversal directions, respectively.

[Example 9]

Co-PET (BELL PET IFG-8L, trade name, product of Kanebo, Ltd., melting point: 226°C), an adhesive resin
5 (SF730, trade name, product of Mitsui petrochemical Industries, Ltd.), a mixture of 60 wt.% of nylon 6 (AMILAN CM6001, trade name, product of Toray Industries, Inc.) and 40 wt.% of nylon 6/6I (SNIAMID F36T, trade name, product of Caffaro Co., LTD., Tm: 220°C), EVOH (EP-S105A, 10 trade name, product of Kuraray Co., Ltd.), and VLDPE (EXCELLEN VL401, trade name, product of Sumitomo Chemical Co., Ltd.) were co-extruded into a tube having the following layer structure by means of 5 extruders, thereby obtaining a cold parison (non-oriented multi-layer tube). The cold parison was then heated again and stretched each about 2.9-3.0 times in machine and transversal directions by an inflation method. The thus-obtained tubular film was cut in the take-up direction of the film, thereby obtaining a film having a width between 15 folds of 450 mm. This film was filled with processed meat by a pillow packaging machine, sealed and cut into predetermined lengths. Thereafter, the resultant packages were heated at 90°C for 1 minute to shrink the film. As a result, it was found that the film has smooth 20 suitability for the automatic packaging machine, beautifully fits on the processed meat after boiling the package, and has superior surface gloss.

The layer structure of the film was as follows:

outer layer (co-PET; 2 μm)/adhesive layer (1 μm)/
intermediate layer (mixture of 60 wt.% of nylon 6 and 40
wt.% of nylon 6/6I; 6 μm)/intermediate layer (EVOH; 5
5 μm)/adhesive layer (1 μm)/inner layer (VLDPE; 18 μm).

This multi-layer film had good stretchability
(rank: ○), an oxygen transmission rate of 90
 $\text{cm}^3/\text{m}^2 \cdot \text{day} \cdot \text{atm}$ and hot-water shrinks of 34% and 32% in
longitudinal and transversal directions, respectively.

10 [Example 10]

A mixture of 90 wt.% of nylon 6 (AMILAN CM1021XF,
trade name, product of Toray Industries, Inc.) and 10
wt.% of nylon 610/MXD6 (ratio of comonomer: 80/20 wt.%,
T_m: 173°C), an adhesive resin (F3100K, trade name,
15 product of Mitsubishi Kagaku Co., Ltd.), VLDPE (EXCELLEN
VL401, trade name, product of Sumitomo Chemical Co.,
Ltd.), and a mixture of 98 wt.% of nylon 6 (AMILAN
CM1021XF, trade name, product of Toray Industries, Inc.)
and 2 wt.% of a lubricant (EEA/CaCO₃ = 94/6 by weight)
20 were co-extruded into a tube having the following layer
structure by means of 4 extruders, thereby obtaining a
cold parison (non-oriented multi-layer tube). The cold
parison was then heated again and stretched 2.5 times and
3.1 times, respectively, in machine and transversal
25 directions by an inflation method, and relaxed at a
temperature of 80°C and a relaxation rate of 5-7%,
thereby obtaining a tubular film having a thickness of

about 50 µm. The tubular film was used as a casing film to conduct a pork sausage-filling experiment in the same manner as in Example 6. The resultant packaged products of pork sausage scarcely vary in dimensions and were 5 beautifully finished.

The layer structure of the film was as follows:
outer layer (mixture of 90 wt.% of nylon 6 and 10 wt.% of
nylon 610/MXD6; 20 µm)/adhesive layer (2 µm)/
intermediate layer (VLDPE; 20 µm)/adhesive layer (2
10 µm)/inner layer (mixture of 98 wt.% of nylon 6 and 2 wt.%
of the lubricant; 5 µm).

This multi-layer film had good stretchability (rank: ○) which has been unable to be achieved by the conventional structure making use of nylon 6, an oxygen 15 transmission rate of 280 cm³/m²·day·atm and hot-water shrinks of 15% and 10% in longitudinal and transversal directions, respectively.

[Example 11]

A non-oriented sheet having the following 7-layer 20 structure was produced by an upward blown-film extrusion process (apparatus: manufactured by BARMAG) using 5 extruders.

- (1) Outer layer: MDPE (grade: LUPOLEN 3020F, product of BASF);
- 25 (2) Adhesive layer: 15 wt.% of adhesive resin (grade: OREVAC, product of ATO-CHEM) and 85 wt.% of LDPE (grade: ATTANE, product of DOW CHEMICAL);

(3) Intermediate layer:

- ① Nylon 6/66 (grade: ULTRAMID C35F, product of BAYER),
- ② Mixture of 80 wt.% of nylon MXD6 (grade: MXD6 6007K, product of Mitsubishi Gas Chemical Company, Inc.) and 20 wt.% of nylon 6/12/MXD6 (that described above),

- 5 ③ Nylon 6/66 (that described above);

(4) Adhesive layer: 15 wt.% of adhesive resin (grade: OREVAC, product of ATO-CHEM) and 85 wt.% of LDPE (grade: ATTANE, product of DOW CHEMICAL);

10 (5) Inner layer: MDPE (that described above).

The multi-layer sheet thus obtained had a thickness of 140 µm in total and was composed of the outer layer (20 µm)/adhesive layer (8 µm)/intermediate layers (15/15/15 µm)/adhesive layer (8 µm)/inner layer (59 µm).

15 The multi-layer sheet of this laminated structure had stable suitability for blown-film extrusion and was able to be produced at a production line speed at least 1.3 times as fast as that of the multi-layer sheet obtained in Comparative Example 6 which will be described subsequently. The multi-layer sheet was heated at 100°C 20 for 2 seconds by a deep-drawing machine and then deep drawn under a gauge pressure of 0.3 MPa. As a result, a container having a diameter of 100 mm and a depth of 30 mm could be obtained.

25 [Example 12]

A multi-layer sheet was produced in the same manner as in Example 11 except that the intermediate layers were

changed to ① a mixture of 95 wt.% of nylon 6 (grade: DURETHANE B35FKA, product of BASF) and 5 wt.% of nylon 6/12/MXD6 (that described above), ② a mixture of 85 wt.% of nylon MXD6 (that described above) and 15 wt.% of nylon 6/12/MXD6 (that described above), and ③ a mixture of 95 wt.% of nylon 6 (that described above) and 5 wt.% of nylon 6/12/MXD6 (that described above).

The multi-layer sheet of this laminated structure had stable suitability for blown-film extrusion and was able to be produced at a production line speed at least 1.3 times as fast as that of the multi-layer sheet obtained in Comparative Example 6 which will be described subsequently. The multi-layer sheet was heated at 100°C for 2 seconds by a deep-drawing machine and then deep drawn under a gauge pressure of 0.3 MPa. As a result, a container having a diameter of 100 mm and a depth of 30 mm could be obtained.

[Example 13]

A multi-layer sheet was produced in the same manner as in Example 11 except that the intermediate layers were changed to ① a mixture of 90 wt.% of nylon 6 (that described above) and 10 wt.% of nylon 6/12/MXD6 (that described above), ② nylon MXD6 (that described above), and ③ a mixture of 90 wt.% of nylon 6 (that described above) and 10 wt.% of nylon 6/12/MXD6 (that described above).

The multi-layer sheet of this laminated structure

had stable suitability for blown-film extrusion. The multi-layer sheet was heated at 100°C for 2 seconds by a deep-drawing machine and then deep drawn under a gauge pressure of 0.3 MPa. As a result, a container having a 5 diameter of 100 mm and a depth of 30 mm could be obtained.

[Comparative Example 6]

A multi-layer sheet was produced in the same manner as in Example 11 except that the intermediate layers were changed to ① nylon 6 (that described above), ② nylon 10 MXD6 (that described above), and ③ nylon 6 (that described above). The multi-layer sheet was somewhat difficult to be deep drawn.

[Example 14]

A multi-layer sheet was produced in the same manner 15 as in Example 11 except that the intermediate layers were changed to ① a mixture of 90 wt.% of nylon 6 (that described above) and 10 wt.% of nylon 6/12/MXD6 (that described above), ② EVOH (that described above), and ③ a mixture of 90 wt.% of nylon 6 (that described above) and 20 10 wt.% of nylon 6/12/MXD6 (that described above), and the thickness and structure of the sheet were changed as follows.

The multi-layer sheet thus obtained had a thickness of 140 µm in total and was composed of the outer layer 25 (20 µm)/adhesive layer (8 µm)/intermediate layers (18/10/18 µm)/adhesive layer (8 µm)/inner layer (58 µm).

The multi-layer sheet of this structure had stable

suitability for blown-film extrusion and was able to be produced at a production line speed at least 1.4 times as fast as that of the multi-layer sheet obtained in Comparative Example 7 which will be described 5 subsequently. The thus-obtained tubular film was cut in the take-up direction of the film, thereby obtaining a film having a width between folds of 400 mm. This film was filled with processed meat by a pillow packaging machine, sealed and cut into predetermined lengths. As a 10 result, it was found that the film has smooth suitability for the automatic packaging machine. The multi-layer sheet was soft to the touch, which has been achieved by the conventional films or sheets of this type, and was well balanced between the suitability for packaging 15 machines and softness.

[Comparative Example 7]

A multi-layer sheet was produced in the same manner as in Example 14 except that the intermediate layers were changed to ① nylon 6 (that described above), ② EVOH 20 (that described above) and ③ nylon 6 (that described above). (See Example 14 as to the evaluation of this multi-layer sheet)

CLAIMS

1. A single-layer or multi-layer packaging film or sheet having at least one layer formed of a polyamide resin composition, wherein the layer formed of the polyamide resin composition is a layer (A) formed of a polyamide resin composition comprising a copolymer nylon (c) composed of an aliphatic nylon (co)polymer component (1) and an aromatic nylon (co)polymer component (2) in a proportion of at least 5 wt.%.

2. The packaging film or sheet according to Claim 1, wherein the polyamide resin composition layer (A) is a layer formed of a polyamide resin composition comprising at least 5 wt.% of the copolymer nylon (c) and at most 95 wt.% of another nylon (co)polymer than the copolymer nylon (c).

3. The packaging film or sheet according to Claim 1, wherein the aromatic nylon (co)polymer component (2) in the copolymer nylon (c) has an aromatic diamine unit.

4. The packaging film or sheet according to Claim 1, wherein the aromatic nylon (co)polymer component (2) in the copolymer nylon (c) has an aromatic dicarboxylic acid unit.

5. The packaging film or sheet according to Claim 1,

wherein a proportion of the aromatic nylon (co)polymer component (2) to be copolymerized in the copolymer nylon (c) is at most 40 wt.%.

5 6. The packaging film or sheet according to Claim
3, wherein the copolymer nylon (c) is a copolymer nylon comprising ① 60-96 wt.% of the aliphatic nylon (co)polymer component and ② 4-40 wt.% of an aromatic nylon component containing a xylylenediamine unit as the
10 aromatic nylon (co)polymer component.

7. The packaging film or sheet according to Claim
3, wherein the copolymer nylon (c) is a copolymer nylon comprising ① 45-92 wt.% of at least one aliphatic nylon component selected from the group consisting of the components of nylon 6, nylon 66 and nylon 610 and ② 4-25 wt.% of another aliphatic nylon component than the component ① as the aliphatic nylon copolymer component, and ③ 4-40 wt.% of an aromatic nylon component
20 containing a xylylenediamine unit as the aromatic nylon (co)polymer component.

8. The packaging film or sheet according to Claim
4, wherein the copolymer nylon (c) is a copolymer nylon
25 comprising ① 60-96 wt.% of the aliphatic nylon (co)polymer component and ② 4-40 wt.% of a polycondensate component of hexamethylenediamine with at

least one aromatic dicarboxylic acid selected from the group consisting of isophthalic acid and terephthalic acid as the aromatic nylon (co)polymer component.

5 9. The packaging film or sheet according to Claim 1, wherein the polyamide resin composition layer (A) is a layer formed of a polyamide resin composition comprising at least one nylon selected from the group consisting of nylon 6 (a) and amorphous nylon (b).

10 10. The packaging film or sheet according to Claim 9, wherein the polyamide resin composition layer (A) is a layer formed of a polyamide resin composition comprising 40-70 wt.% of nylon 6 (a), 5-20 wt.% of an amorphous 15 nylon (b), 5-30 wt.% of the copolymer nylon (c) and 10-30 wt.% of a polyolefin resin (d).

20 11. The packaging film or sheet according to Claim 9, wherein the polyamide resin composition layer (A) is a layer formed of a polyamide resin composition comprising 50-95 wt.% of nylon 6 (a) and 5-50 wt.% of the copolymer 25 nylon (c).

12. The packaging film or sheet according to Claim 1, wherein the polyamide resin composition layer (A) is a layer formed of a polyamide resin composition comprising 50-95 wt.% of nylon MXD6 (e) and 5-50 wt.% of the

copolymer nylon (c).

13. The packaging film or sheet according to any one of Claims 1 to 12, which is a single-layer oriented
5 film or sheet composed of the polyamide resin composition layer (A).

14. The packaging film or sheet according to any one of Claims 1 to 12, which is a multi-layer oriented
10 film or sheet comprising at least one polyamide resin composition layer (A).

15. The packaging film or sheet according to Claim 14, wherein at least one polyamide resin composition
15 layer (A) is provided as an intermediate layer.

16. The packaging film or sheet according to Claim 15, wherein at least one polyamide resin composition layer (A) is provided as an intermediate layer, and
20 polyolefin resin layers are provided as the outermost and innermost layers through adhesive resin layers.

17. The packaging film or sheet according to Claim 15, wherein at least one polyamide resin composition
25 layer (A) is provided as an intermediate layer, and a polyethylene terephthalate resin layer and a polyolefin resin layer are provided as one surface layer and the

other surface layer, respectively, through adhesive resin layers.

18. The packaging film or sheet according to Claim
5 14, wherein the polyamide resin composition layer (A) is provided as at least one surface layer.

19. The packaging film or sheet according to Claim
18, wherein a polyolefin resin layer is provided as an
10 intermediate layer.

20. The packaging film or sheet according to Claim
18, wherein the polyamide resin composition layer (A) is provided as at least one surface layer, and a polyamide
15 layer is provided as the other surface layer.

21. The packaging film or sheet according to Claim
14, which has a layer structure that at least one
polyamide resin composition layer (A) is provided in
20 adjacency with at least one of at least one polyamide
resin layer and at least one gas barrier resin layer.

22. The packaging film or sheet according to any
one of Claims 1 to 12, which is a non-oriented film or
25 sheet comprising at least one polyamide resin composition
layer (A).

23. The packaging film or sheet according to Claim 22, wherein at least one polyamide resin composition layer (A) is provided as an intermediate layer.

5 24. The packaging film or sheet according to Claim 23, wherein at least one polyamide resin composition layer (A) is provided as an intermediate layer, and polyolefin resin layers are provided as the outermost and innermost layers through adhesive resin layers.

10

25. The packaging film or sheet according to Claim 23, wherein at least one polyamide resin composition layer (A) is provided as an intermediate layer, and a polyethylene terephthalate resin layer and a polyolefin resin layer are provided as one surface layer and the other surface layer, respectively, through adhesive resin layers.

26. The packaging film or sheet according to Claim 22, wherein the polyamide resin composition layer (A) is provided as at least one surface layer.

27. The packaging film or sheet according to Claim 26, wherein a polyolefin resin layer is provided as an intermediate layer.

28. The packaging film or sheet according to Claim

26, wherein the polyamide resin composition layer (A) is provided as at least one surface layer, and a polyamide layer is provided as the other surface layer.

5 29. The packaging film or sheet according to Claim 22, which has a layer structure that at least one polyamide resin composition layer (A) is provided in adjacency with at least one of at least one polyamide resin layer and at least one gas barrier resin layer.

10

30. A multi-layer packaging film or sheet having a layer structure that at least two layers of a layer formed of a copolymer nylon (c) composed of an aliphatic nylon (co)polymer component (1) and an aromatic nylon (co)polymer component (2), and a layer formed of another polyamide resin than the copolymer nylon (c) are provided in adjacency with each other.

31. A multi-layer packaging film or sheet having a layer structure composed of at least two layers of a layer formed of a polyamide resin composition comprising a copolymer nylon (c) composed of an aliphatic nylon (co)polymer component (1) and an aromatic nylon (co)polymer component (2) having an aromatic diamine unit, and at least one layer of a layer formed of another polyamide resin composition than the above composition and a gas barrier resin layer.

32. The packaging film or sheet according to Claim 1, which has an oxygen transmission rate of 300 cm³/m²·day·atm or smaller.

5 33. The packaging film or sheet according to Claim 1, which is an oriented film and has a hot-water shrink of at least 5%.

10 34. The packaging film or sheet according to Claim 1, which is a casing film.

15 35. The packaging film or sheet according to Claim 22, which is a film or sheet suitable for deep-draw packaging.

36. The packaging film according to Claim 14, which is a film suitable for pillow packaging.

20 37. The packaging film or sheet according to Claim 22, which is a film or sheet suitable for pillow packaging.

25 38. A single-layer or multi-layer blow molded container having at least one layer formed of a polyamide resin composition, wherein the layer formed of the polyamide resin composition is a layer (A) formed of a polyamide resin composition comprising a copolymer nylon

(c) composed of an aliphatic nylon (co)polymer component (1) and an aromatic nylon (co)polymer component (2) in a proportion of at least 5 wt.%, or of the copolymer nylon (c) alone.

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/JP 97/04787

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 B32B27/34 B32B27/08 C08L77/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 B32B C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 43 39 337 A (NATURIN) 24 May 1995 see claims; examples ---	1-31,38
X	WO 95 07180 A (ALLIED SIGNAL) 16 March 1995 see claims ---	1-31,38
X	EP 0 527 237 A (MITSUBISHI KASEI POLYTEC) 17 February 1993 see claims; examples ---	1-31,38
X	EP 0 465 931 A (GUNZE) 15 January 1992 see claims ---	1,9,10
X	EP 0 714 763 A (IDEMITSU PETROCHEMICAL) 5 June 1996 see claims; examples ---	1-31,38
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

1

Date of the actual completion of the international search

17 March 1998

Date of mailing of the international search report

06.04.1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Boeker, R

INTERNATIONAL SEARCH REPORT

Internal Application No	PCT/JP 97/04787
-------------------------	-----------------

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 39 43 024 A (HOECHST) 4 July 1991 see claims & JP 04 122 732 A cited in the application -----	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal ref Application No

PCT/JP 97/04787

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE 4339337 A	24-05-95	BR 9405983 A WO 9513707 A EP 0682476 A ES 2080041 T JP 8505781 T US 5612104 A		06-02-96 26-05-95 22-11-95 01-02-96 25-06-96 18-03-97
WO 9507180 A	16-03-95	US 5547765 A CA 2168864 A DE 717678 T EP 0717678 A ES 2091166 T JP 9504748 T		20-08-96 16-03-95 30-01-97 26-06-96 01-11-96 13-05-97
EP 0527237 A	17-02-93	JP 5000492 A AU 646331 B AU 1337892 A WO 9215455 A JP 5077373 A		08-01-93 17-02-94 06-10-92 17-09-92 30-03-93
EP 0465931 A	15-01-92	JP 4059244 A JP 4185322 A AU 643035 B AU 7929991 A DE 69119982 D DE 69119982 T ES 2087179 T NZ 238706 A US 5562996 A US 5688456 A		26-02-92 02-07-92 04-11-93 02-01-92 11-07-96 24-10-96 16-07-96 22-12-94 08-10-96 18-11-97
EP 0714763 A	05-06-96	CN 1143569 A JP 8224844 A US 5716696 A		26-02-97 03-09-96 10-02-98
DE 3943024 A	04-07-91	JP 4122732 A NL 9002547 A US 5326613 A		23-04-92 16-07-91 05-07-94